

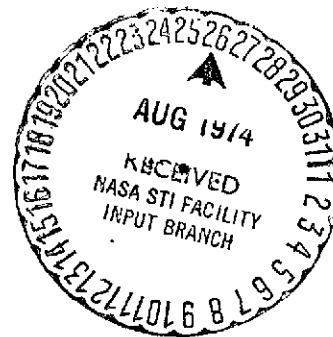
FINAL REPORT ON

Development of a Global Pollution Model For  
CO, CH<sub>4</sub>, and CH<sub>2</sub>O

by

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ABSTRACT

The remote sensing of atmospheric pollutants from satellites will be feasible within the next few years. To effectively interpret these data, global pollution models that describe the transport and the physical and chemical processes occurring between sources and sinks of pollution are essential. This report describes the current status of a global pollution model for carbon monoxide, methane, and formaldehyde.

The study considers the physico-chemical action of these three pollutants in the troposphere. This geographic restriction is convenient since the tropopause provides a natural boundary across which little transport occurs. The data on sources and sinks for these pollutants is based on available information and assumptions relative to the major man-made and natural contributions. The distributions and concentrations of methane, formaldehyde, and carbon monoxide in the atmosphere are interrelated by the chemical reactions in which they participate. A chemical kinetic model based on the pseudo-steady state approximation for the intermediate species has been developed to account for these reactions.

The numerical procedure being used to mathematically describe the pollution transport is a mass conservative scheme employing an integral flux approach. It is fourth-order accurate in space which is desirable in simulating convective

processes in three space dimensions. Since computer storage places restrictions on the scale of transport processes that are explicitly calculated, smaller scale mixing is described using an artificial diffusivity.

At the present, the computer model is successfully functioning for short time integrations. Some additional work remains to develop a plotting routine and to generate a realistic modeling parameter data tape.

## INTRODUCTION

In the MAPS (Measurement of Air Pollution from Satellites) experiment proposed for NIMBUS G by Reichle<sup>(1)</sup>, the global distributions of carbon monoxide, sulfur dioxide, nitrogen dioxide, methane, ammonia, and aerosols would be measured over a two year period. The utility of satellite remote sensing data of pollutants will be greatly enhanced if meaningful global models of pollution are developed. These models will be required to realistically analyze the atmospheric transport of pollution from its sources to sinks. Furthermore, these models can be significant in placing anthropogenic sources in proper perspective on a global scale. This report briefly describes the development and current status of a tropospheric global model for carbon monoxide (CO), methane, ( $\text{CH}_4$ ), and formaldehyde ( $\text{CH}_2\text{O}$ ).

The analysis is accomplished by geographically distributing the sources and sinks of CO,  $\text{CH}_4$ , and  $\text{CH}_2\text{O}$ , and simulating their convective and diffusive transport by a numerical solution on the computer of the turbulent diffusion equation. The atmospheric phenomena of these three species are coupled through atmospheric chemical reactions that occur. Thus, the three species must be considered simultaneously. Generally speaking, the oxidation of methane produces formaldehyde which decomposes to carbon monoxide. Other sources and sinks of these pollutants are also operating.

Other analyses to the present have utilized a global residence time approach<sup>(2,3,4,5,6,e.g.)</sup>. Models incorporating a multiplicity of sources and sinks have not, to the author's knowledge, been attempted. The model outlined

in this study employs known source and sink strength data, the atmospheric chemistry of the pollutants in question, monthly averaged climatological data, and the turbulent diffusion equation for each species to establish global concentration distributions.

#### GENERAL MODEL DESCRIPTION

The model development is restricted to the troposphere. This is a logical boundary since the tropopause provides a natural surface thru which the rate of mass transfer is relatively low. Furthermore, the photolytic decomposition of CO<sub>2</sub> appears to be unimportant as a source of CO in the troposphere<sup>(7)</sup>, and this enables one to decouple the CO transport from the CO<sub>2</sub> transport.

#### Sources and Sinks of CH<sub>4</sub>

The sources and sinks of methane appear to be reasonably well understood at the present. The anthropogenic sources are largely the result of internal combustion engines and oil drilling and refinery operations. These emissions can be fairly well mapped based on automobile density and industrial activities.

The natural sources apparently far out strip the man made sources - the principal ones being decaying vegetation and other biological action. Some of this biological action occurs within marine environments, and as a result the surface waters of the oceans, bays, and rivers appear to be supersaturated with methane. Lamontagne, Swinnerton, Linnenbom, and Smith<sup>(8)</sup> have reported equivalent surface ocean and sea water concentrations about 1.2 to 1.7 times the corresponding atmospheric concentrations. Specifically in open tropical

ocean waters, the surface concentrations ( $4.7 \times 10^{-5}$  ml/l) corresponded to an equilibrium atmospheric concentration of 1.80 ppm whereas the measured atmospheric concentrations averaged 1.38 ppm. Bay and river waters appear to be even more heavily supersaturated. Their results specifically cited the following supersaturation ratios: Chesapeake Bay - 14.3, York River - 21.2, Mississippi River - 5.67, Potomac River - 36.0. These values may also be affected by local pollution problems. The data of Brooks and Sackett<sup>(9)</sup> on the coastal waters of the Gulf of Mexico generally support Lamontagne et al's results. However, they report that in the Yucutan area, where there is a major upwelling of deep water with low hydrocarbon concentration, the Gulf of Mexico acts as a sink for methane.

The principal sink mechanism for methane appears to be in the homogeneous gas phase reaction of methane with hydroxyl radicals.



The methyl radical can subsequently undergo reactions which results in formaldehyde and ultimately in CO formation. Thus, this sink for methane provides one natural source for formaldehyde and carbon monoxide. The following sequence of reactions is responsible for producing the hydroxyl radical<sup>(3)</sup>:

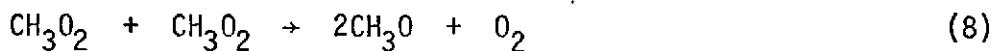
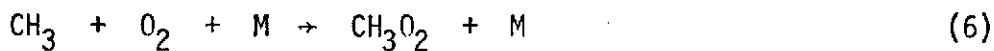
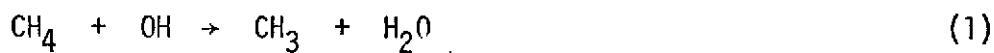


It will be noted later that the hydroxyl and atomic oxygen (O) are also important in reactions with CO.

## Sources and Sinks of CH<sub>2</sub>O

The anthropogenic sources of formaldehyde appear to be relatively small - the main ones being direct emission from automobile exhaust and formation during photochemical smog episodes. These estimates can be fairly reliably based on past auto exhaust emission estimates and studies.

The only apparent natural source for CH<sub>2</sub>O is from the methane oxidation just cited. Levy<sup>(10,11)</sup> and McConnell, McElroy, and Wofsy<sup>(12)</sup> have suggested the following steps in the formation of formaldehyde by this mechanism.



Thus, the formaldehyde formation and concentration is directly coupled to the methane distribution.

The main sink of formaldehyde is in photochemical decomposition and the reaction with hydroxyl radicals. The following reactions appear to be important<sup>(10,11,12)</sup>.



The production of CHO also leads to carbon monoxide formation via<sup>(13,14)</sup>



Therefore, the source and sink distribution of formaldehyde is primarily due to homogeneous gas phase reactions and is coupled to the methane and carbon monoxide distributions.

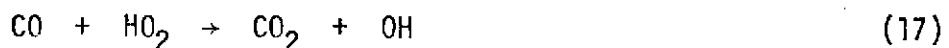
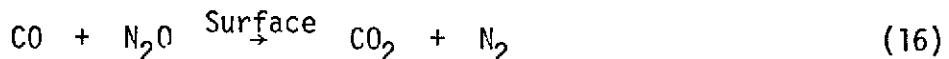
#### Sources and Sinks of CO

The sources, sinks, and concentrations of carbon monoxide have been summarized by Bortner, Kummier, and Jaffe<sup>(3)</sup>. The world-wide anthropogenic sources are estimated to be slightly in excess of 300 million tons/year with nearly two-thirds resulting from motor vehicle emissions. The remainder is distributed between stationary combustion sources, industrial processing, and incineration. Therefore, these sources would be distributed largely according to motor vehicle density.

The major natural sources of carbon monoxide appear to be the oceans, forest fires, terpene photochemistry, and gas phase reactions. The studies of Junge, Seiler, and Warneck<sup>(5)</sup>, Seiler and Junge<sup>(15)</sup>, Swinnerton, Linnenbom, and Check<sup>(16)</sup>, and Lamontagne, Swinnerton, and Linnenbom<sup>(17)</sup> indicate that the level of excess CO in the ocean corresponds to an equilibrium air phase concentration of about 3.5 ppm. These data were obtained during ocean cruises. It is, of course, reasonable to expect that the river, lake, or ocean regions near urban areas, where the CO concentrations may be considerably larger than 3.5 ppm, may act as a sink for CO. Furthermore, it is possible that the oceans at the

high latitudes serve as a sink for CO produced by oceans at the low latitudes since the warmer tropical waters would likely have a higher biological activity producing more CO. With the warmer water, the solubility of CO is reduced. Transport over colder waters with greater CO solubility capacity then creates the possibility of these sections acting as a sink for CO. Thus, it is plausible that the oceans act as both a source and sink for CO. Similar arguments could be made for methane.

In addition to terpene photochemistry and forest fires (combined sources are estimated at  $23 \times 10^6$  ton/year<sup>(18)</sup>), the other principal natural source of CO appears to be the gas phase reactions cited earlier. However, these cannot be divorced from the reactions which consume CO, of which the following seem to be important<sup>(3)</sup>.



Reaction (16)<sup>(19,20,21,22,23)</sup> is reportedly first order in CO but zeroth order in N<sub>2</sub>O. This is a surface catalyzed reaction and requires, for complete accuracy, detailed information on the atmospheric aerosol as to size distribution and chemical composition. Reaction (17) has been suggested by Westenberg<sup>(24)</sup> to be important in atmospheric pollution problems. However, the results of Davis, Wong, Payne, and Stief<sup>(25)</sup> indicate that it is unimportant in the overall oxidation processes of CO. As a result, the current model ignores Reaction (17).

Another natural sink of CO of seemingly large significance is the soil. The recent work of Inman<sup>(26)</sup>, Inman, Ingersoll, and Levy<sup>(27)</sup>, and Ingersoll and Inman<sup>(28)</sup> point up this significance. Recent field studies in which soils were exposed *in situ* to test atmospheres containing  $115 \text{ mg m}^{-3}$  CO (100 ppm) showed average uptake rates that varied from  $3.5 \mu\text{g s}^{-1}\text{m}^{-2}$  for desert areas to  $16.5 \mu\text{g s}^{-1}\text{m}^{-2}$  for tropical deciduous forest areas. By using an average concentration driving force of  $57 \text{ mg m}^{-3}$  CO (50 ppm) and assuming conditions of atmospheric pressure and 293 K, the mass transfer coefficient at the surface corresponds to  $0.594 \times 10^{-4} \text{ m s}^{-1}$  and  $2.38 \times 10^{-4} \text{ m s}^{-1}$ , respectively. These values are probably indicative of the rate of the biological reaction that is occurring near the surface of the soil and may simply be representative of the type and concentration of the soil microorganisms utilizing CO. One of the big uncertainties relative to soil scavenging is the determination of which fraction of these microorganisms are anaerobic methane-producing<sup>(29)</sup> and what fraction are aerobic CO<sub>2</sub> producing. Furthermore, Seiler and Junge<sup>(15)</sup> have suggested that at low concentrations (around  $0.23 \text{ mg m}^{-3}$  at 298 K) a temperature dependent equilibrium of CO above soils occurs. If this is truly the case, then the soils can act as either sinks or sources for carbon monoxide in much the same manner as do the oceans.

A source and/or sink common to all three species is leakage from and/or to the stratosphere. Since the initial model is restricted to the troposphere, this leakage is considered as sources and/or sinks. In the specific case of CO, leakage from the troposphere to the stratosphere is reasonable to expect since the CO that escapes thru the tropopause will typically undergo chemical reactions

and not return to the troposphere as CO. This is substantiated by the vertical profiles of CO which show a decrease of CO mixing ratio with height above the tropopause. (30)

The leakage of  $\text{CH}_4$  thru the tropopause would be similar to that for CO since vertical profiles of  $\text{CH}_4$  also show a decrease with increasing altitude above the tropopause<sup>(13,31)</sup>. This type of information has not as yet been found for formaldehyde.

#### CURRENT STATE OF MODEL DEVELOPMENT

The general approach in simulation of the  $\text{CH}_4 - \text{CH}_2\text{O} - \text{CO}$  cycle consists of the following steps:

- a. Initialize the  $\text{CH}_4$ ,  $\text{CH}_2\text{O}$  and CO concentrations in the troposphere.

In order to conserve computer time, the initial concentrations selected are approximately that expected in the atmosphere. This should not affect the final results but simply the time required to reach steady state.

- b. Distribute the sources and sinks of the various species on the Earth's surface and at the tropopause consistent with the physico-chemical considerations. This involves proper interpretation of oceans and lands as sources and/or sinks of the particular species. As a first approximation, the tropopause is being considered as a zero flux boundary. Thus, all pollutant generation and consumption is entirely within the troposphere.

- c. Solve the three coupled unsteady state turbulent diffusion equations for  $\text{CH}_4$ ,  $\text{CH}_2\text{O}$ , and  $\text{CO}$  with the boundary conditions established by b. The appropriate climatological data<sup>(32)</sup> is used to establish the wind field, temperature field, and water vapor field. The coupling of the diffusion equations results from the gas phase reactions creating homogeneous generation terms. This, therefore, accounts for the chemical sources and sinks present. A simplified chemical kinetic model based on the pseudo-steady state approximation for the intermediate species has been developed to account for these reactions.
- d. Continue the integration in time until reasonably steady concentration distributions exist.

The inherent advantage to using this procedure is that one does not presuppose the atmospheric concentrations of the three pollutant species being studied. This, therefore, provides a meaningful test of the distribution of sources and sinks. This should not imply however, that there are not uncertainties present. But these uncertainties are mostly associated with the strengths of the sources and sinks, and a primary goal of satellite remote sensing is to establish the magnitude of these source and sink strengths.

At the present time, the computer program to describe the physico-chemical behavior of the three species is successfully functioning on the computer system at NASA Langley Research Center for short time integrations using restricted modeling parameters. Since the space length scales in the numerical calculation are quite large, the simulation must be continued for relatively

long periods of time. Current results indicate that real time simulation on the order of ten to thirty days is required. Furthermore, computer time to simulation time appears to be on the order of 1:10 to 1:20. Therefore, simulation with one set of modeling parameters will likely require twenty to thirty hours of CDC6600 time. As a result, the possibility of using the NCAR CDC7600, which is approximately five times faster, is being investigated.

To supplement the main calculating program, a data tape incorporating realistic modeling parameters and a computer routine for plotting isopleths of the calculated concentrations are being developed. The successful coordination of the three separate phases should be established before any long term numerical integration is attempted. It is hoped that these studies can be continued.

## REFERENCES

1. Reichle, Henry G., Jr.: MAPS - An Experiment Suggested for NIMBUS G. NASA Langley Research Center, April 2, 1973.
2. McCormac, B. M., Editor: Introduction to the Scientific Study of Atmospheric Pollution. D. Reidel Publishing Co., Dordrecht, Holland, 1971.
3. Bortner, M. H., Kummier, R. H., and Jaffe, L. S.: A Review of Carbon Monoxide Sources, Sinks, and Concentrations in the Earth's Atmosphere: NASA CR - 2081, June 1972.
4. Robinson, E. and Robbins, R. C. Final Report on SRI Project PR 6755, February, 1967.
5. Junge, C., Seiler, W., and Warneck, P.: The Atmospheric  $^{12}\text{CO}$  and  $^{14}\text{CO}$  Budget. J. Geophys. Res., Vol. 76 (1971) pp. 2866 - 2879.
6. Weinstock, B.: Carbon Monoxide Residence Time in the Atmosphere. Science, Vol. 166 (1969) pp. 224-225.
7. Wofsy, S. C., McConnell, J. C., and McElroy, M. B.: "Atmospheric  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{CO}_2$ " in Sources, Sinks, and Concentrations of Carbon Monoxide and Methane in the Earth's Environment. Joint Meeting of The American Geophysical Union and The American Meteorological Society; August 1972.
8. Lamontagne, R. A., Swinnerton, J. W., Linnenbom, V. J., and Smith, W.: "Methane Concentrations in Various Marine Environments" in Sources, Sinks, and Concentrations of Carbon Monoxide and Methane in the Earth's Environment. Joint Meeting of The American Geophysical Union and The American Meteorological Society; August 1972.
9. Brooks, J. M. and Sackett, W. M.: "Light Hydrocarbon Concentrations in the Gulf of Mexico" in Sources, Sinks, and Concentrations of Carbon Monoxide and Methane in the Earth's Environment. Joint Meeting of The American Geophysical Union and The American Meteorological Society; August 1972.
10. Levy, H.: Normal Atmosphere: Large Radical and Formaldehyde Concentrations Predicted. Science, Vol. 173 (1971) pp. 141-143.
11. Levy, H.: "The Tropospheric Budgets for Methane, Carbon Monoxide, and Related Species" in Sources, Sinks, and Concentrations of Carbon Monoxide and Methane in the Earth's Environment. Joint Meeting of The American Geophysical Union and The American Meteorological Society, August 1972.

12. McConnell, J. C., McElroy, M. B., and Wofsy, S. C.: Natural Sources of Atmospheric CO. Nature, Vol. 223 (1971) pp. 187-188.
13. Ehhalt, D. H. and Heidt, L. E.: "Vertical Profiles of CH<sub>4</sub> in the Troposphere and Stratosphere" in Sources, Sinks, and Concentrations of Carbon Monoxide and Methane in the Earth's Environment. Joint Meeting of The American Geophysical Union and The American Meteorological Society; August 1972.
14. Kummier, R. H., and Baurer, T.: "A Temporal Model of Tropospheric Carbon - Hydrogen Chemistry" in Sources, Sinks, and Concentrations of Carbon Monoxide and Methane in the Earth's Environment. Joint Meeting of The American Geophysical Union and The American Meteorological Society; August, 1972.
15. Seiler, W., and Junge, C.: Carbon Monoxide in the Atmosphere. J. Geophys. Res. Vol. 75 (1970) pp. 2217-2226.
16. Swinnerton, J. W., Linnenbom, V. J., and Check, C. H.: A Sensitive Gas Chromatographic Method for Determining Carbon Monoxide in Sea Water. Limnol. Oceanogr., Vol. 13 (1968) pp. 193-195.
17. Lamontagne, R. A., Swinnerton, J. W., and Linnenbom, V. J.: Nonequilibrium of Carbon Monoxide and Methane at the Air - Sea Interface. J. Geophys. Res., Vol. 76 (1971) pp. 5117 - 5121.
18. Rossano, A. T., Jr., Editor: Air Pollution Control Guidebook for Management, Environmental Sciences Services Division, 1969.
19. Madley, D. G., and Strickland - Constable, R. F.: Trans. Faraday Soc., Vol. 34 (1953) p. 1312.
20. Smith, R. N. and Mooi, J.: The Catalytic Oxidation of Carbon Monoxide by Nitrous Oxide on Carbon Surfaces. J. Phys. Chem., Vol. 59 (1955) pp. 814-819.
21. Strickland - Constable, R. F.: Trans. Faraday Soc., Vol. 34 (1938) p. 137.
22. Bawn, C. E. H.: Trans. Faraday Soc., Vol. 31 (1936) p. 461.
23. Krause, A.: Bull. Acad. Polon. Sci. Chem., Vol. 9 (1961) p. 5.
24. Westenburg, A. A.: "The Role of the CO - HO<sub>2</sub> Reaction in the Atmospheric CO Sink" in Sources, Sinks, and Concentrations of Carbon Monoxide and Methane in the Earth's Environment. Joint Meeting of The American Geophysical Union and The American Meteorological Society; August 1972.
25. Davis, D. D., Wong, W., Payne, W. A., and Stief, L. J.: "A Kinetics Study to Determine the Importance of HO<sub>2</sub> in Atmospheric Chemical Dynamics: Reaction with CO" in Sources, Sinks, and Concentrations of Carbon Monoxide and Methane in the Earth's Environment. Joint Meeting of The American Geophysical Union and The American Meteorological Society; August 1972.

26. Inman, R. E.: Automotive Air Pollution Research Symposium; Chicago, Illinois; May 1971.
27. Inman, R. E., Ingersoll, R. B., and Levy, E. A.: Science, Vol. 172 (1971), p. 1229
28. Ingersoll, R. B. and Inman, R. E.: "Soil as a Sink for Atmospheric Carbon Monoxide" in Sources, Sinks, and Concentrations of Carbon Monoxide and Methane in the Earth's Environment. Joint Meeting of The American Geophysical Union and The American Meteorological Society; August 1972.
29. Schenellen, C.: Doctoral Thesis, Delft, Rotterdam, 1947 (Cited in Reference 3).
30. Goldman, A., Murcray, D. G., Murcray, F. H., Williams, W. J., Brooks, J. N., Bradford, C. M.: "Vertical Distribution of CO in the Atmosphere" in Sources, Sinks, and Concentrations of Carbon Monoxide and Methane in the Earth's Environment. Joint Meeting of The American Geophysical Union and The American Meteorological Society; August 1972.
31. Ackerman, M. and Muller, C.: "Stratospheric Methane from Infrared Spectra" in Sources, Sinks, and Concentrations of Carbon Monoxide and Methane in the Earth's Environment. Joint Meeting of The American Geophysical Union and The American Meteorological Society; August 1972.
32. Jenne, R. L.: Northern Hemisphere Climatological Grid Data Tape. National Center for Atmospheric Research; July 1969.